Synthesis of new hyperbranched phosphorus-containing polyesters starting from Boltorn H20

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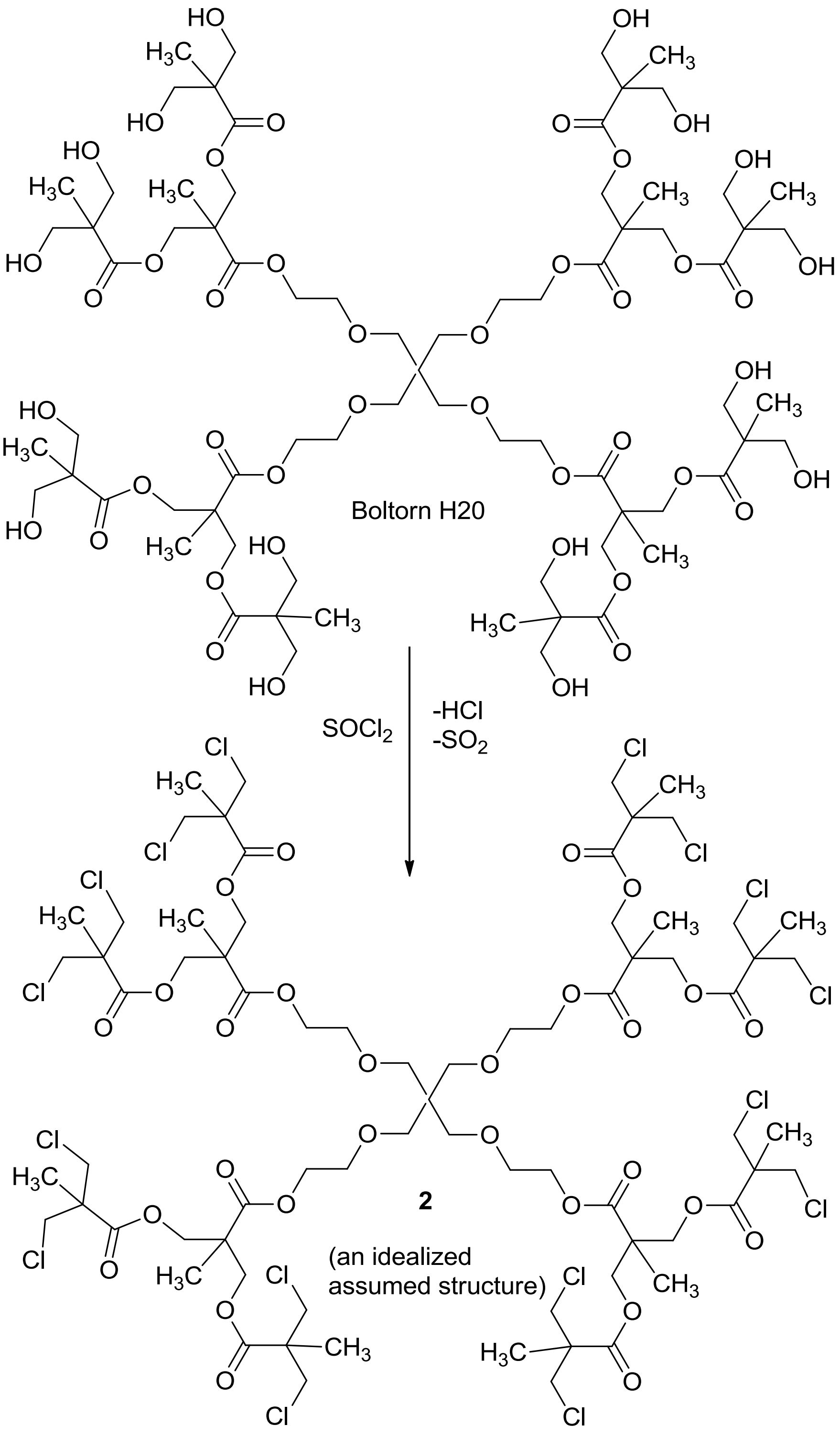
Abstract: Upon gentle treatment with $SOCl_2$, hyperbranched polyester Boltorn H20 afforded a mixture of terminal polychlorides. The latter react with an excess of triphenylphosphine in boiling toluene or with pyridine to give a mixture of polyesters with terminal triphenylphosphonium and pyridinium fragments, respectively.

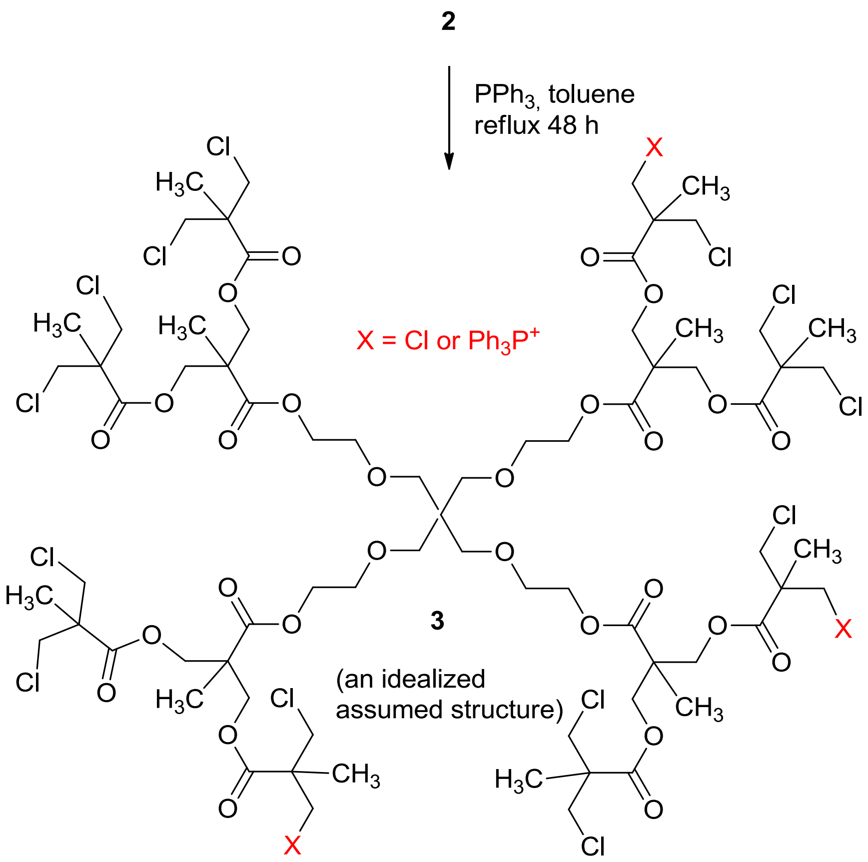
Keywords: *Boltorn H20, hyperbranched polyesters, phosphonium chlorides*.

The wide application of bipolar membrane electrodialysis has aroused an interest in asymmetric bipolar membranes (ABMs) with cation-exchange and anion-exchange layers. A key feature of such membranes is that they partially desalt the solution not only adjust the pH value. Such a bifunctionality of ABMs is responsible for low efficiency of ABMs in the production of strong acids and alkalis. Meanwhile, the bifunctionality of ABMs makes them promising for adjustment of pH of dilute electrolyte solutions. The main limitation of a more common use of ABM-based electrodialysis for pH adjustment processes in solutions is the high overvoltage across ABMs operating in the hydrogen and hydroxyl ion generation mode. To overcome these disadvantages and improve the electrochemical properties, a method of ABMs modification by introducing ionic polymers with catalytic activity in water dissociation into the bipolar region was proposed [1-7]. Hyperbranched polymers such as Boltorn H20 are promising precursors for these catalysts. A significant advantage of hyperbranched polymers is that the number of reactive terminal groups in them is substantially larger than that in linear polymers. To make these polymers catalytically active in water dissociation, they have to be subjected to chemical functionalization. Here we propose the modification of Boltorn H20 leading to the preparation of positively charged hyperbranched species having a catalytic activity in water dissociation. First, Boltorn H20 was treated with $SOCl_2$ under mild conditions (either in 1,4-dioxane or in pure thionyl chloride) to give polychloride **2** (Scheme 1):

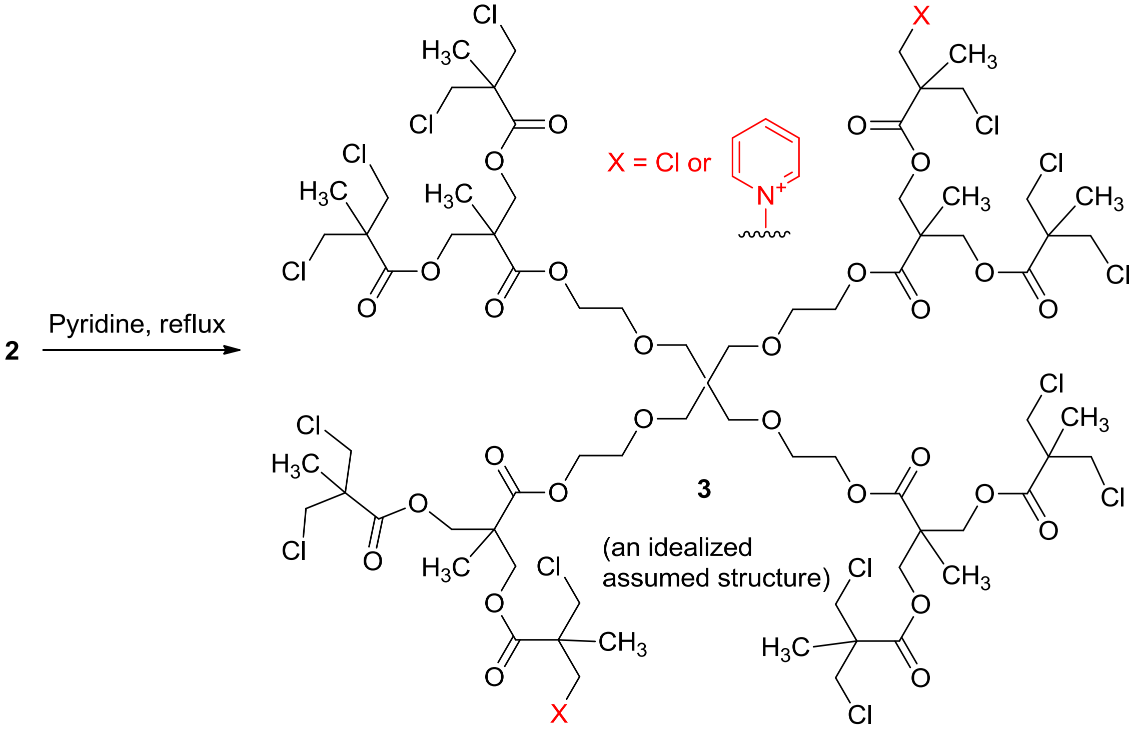


The reaction proceeds at 10-20 °C (external cooling) and is accompanied by evolution of HCl and SO_2; after 24 h the reaction was quenched with water to give polychloride **2** (an idealized assumed structure is presented in Scheme 1) as white precipitate insoluble in water, but soluble in nonpolar solvents. Next, to produce polycharged hyperbranched molecules, polychloride **2** was treated with a) an excess of triphenyl phosphine in boiling toluene; and b) with boiling pyridine. The reaction with PPh_3 resulted in the formation of clear solution which was evaporated to give colorless gummy residue. An excess of PPh_3 was removed by treatment with cold ether. The NMR ^{1}H analysis revealed that the product **3** is a mixture of phosphonium salts having different number of phosphonium groups (1-3) (Scheme 2). The reaction with pyridine resulted in the formation of dark solution, which was evaporated under reduced pressure to give light-brown material, which was treated with cold ether to remove the traces of pyridine.

Scheme 2



The NMR ^{1}H spectrum of pyridinium product **4** (Scheme 3, Fig.1) revealed the presence of 1-2 pyridinium moieties per molecule, along with typical signals of Boltorn H20 core unit. The detailed analysis of NMR, IR and HRMS data will be reported elsewhere. Scheme 3:



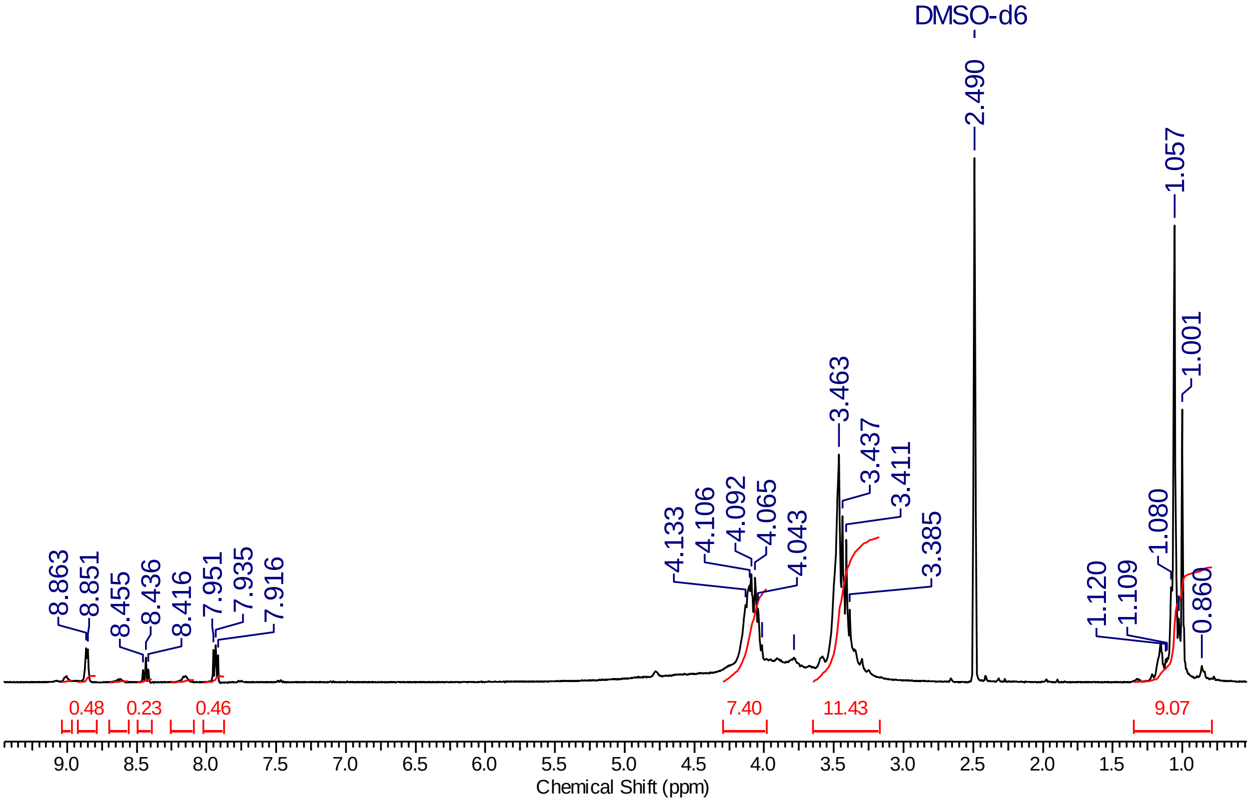


Figure 1. The NMR ^{1}H spectrum of pyridinium product **4** (400 MHz, DMSO-d_6)

Conclusion

We have developed an approach to the synthesis of hyperbranched polyesters bearing terminal triphenylphosphonium and pyridinium fragments, starting from commercially available hyperbranched polyester Boltorn H20. The prepared compounds are useful in the preparation of asymmetric bipolar membranes. The properties of membranes and detailed procedures will be reported elsewhere.

References

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